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(71) Anmelder:
L. & C. Steinmüller GmbH, 51643 Gummersbach, DE

(72) Erfinder:
Klein, Marton, Dr., 51643 Gummersbach, DE;
Kubisa, Ryszard, Dr., 51645 Gummersbach, DE

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

Prüfungsantrag gem. § 44 PatG ist gestellt

(54) Verfahren zur Herstellung von Salpetersäure und Vorrichtung zur Durchführung des Verfahrens

(57) Bei einem Verfahren zur Herstellung von Salpetersäure, bei dem Ammoniak an mindestens einem Katalysatornetz, insbesondere Platinnetz, unter Zufuhr von Sauerstoff verbrannt wird und die Reaktionsgase gekühlt werden, ist zur Vermeidung der Freisetzung von Lachgas vorgesehen, daß die Reaktionsgase stromab des Katalysatornetzes vor der Kühlung über einen temperaturstabilen Katalysator für die Umwandlung des in den Reaktionsgasen enthaltenen N_2O geführt werden.

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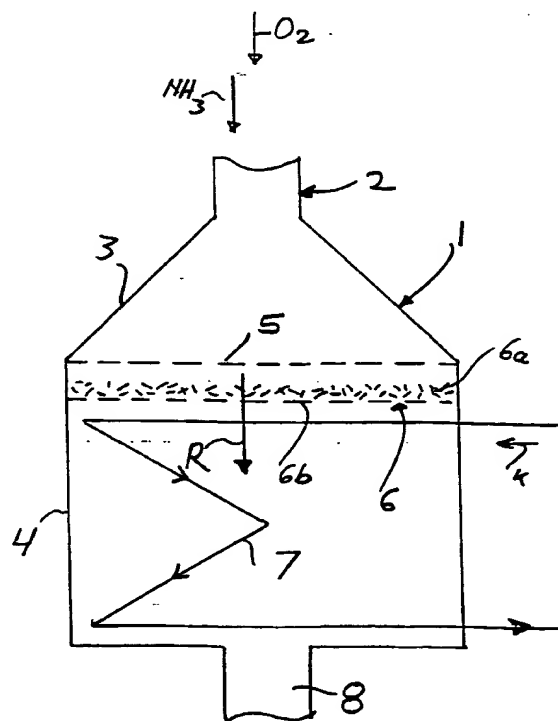
Beschreibung

Die Erfindung betrifft ein Verfahren zur Herstellung von Salpetersäure, bei dem Ammoniak an mindestens einem Katalysatornetz, insbesondere Platinnetz, unter Zufuhr von Sauerstoff verbrannt wird und die Reaktionsgase gekühlt werden.

Die Verbrennung von NH_3 an einem Katalysatornetz erfolgt bei Temperaturen von z. B. 800 bis 1000 °C gemäß der nachfolgenden Gleichung:

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \quad (1).$$
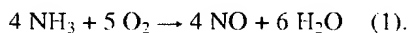
Das hierbei entstehende NO_2 reagiert während und nach der Abkühlung der Reaktionsgase auf ca. 20 bis 30°C mit Sauerstoff zu NO_2:

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \quad (2).$$
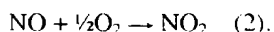
Bei Kontakt mit Wasser und Sauerstoff entsteht die gewünschte Salpetersäure HNO_3:

$$4\,NO_2 + 2\,H_2O + O_2 \rightarrow 4\,HNO_3 \quad (3).$$
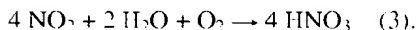
Es wurde gefunden, daß als Nebenreaktion bei der katalytischen NH_3-Verbrennung zu NO nach Gleichung (1) auch unerwünschtes N_2O (Lachgas) entsteht:

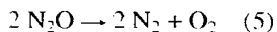$$4\,NH_3 + 4\,O_2 \rightarrow 2\,N_2O + 6\,H_2O \quad (4),$$
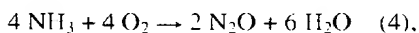
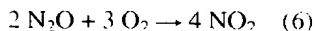welches in den nachfolgenden Stufen der Salpetersäureherstellung nicht abgebaut wird.

Es ist daher die Aufgabe der vorliegenden Erfindung, ein Verfahren anzugeben, bei dem bei der Erzeugung von Salpetersäure eine Freisetzung von Lachgas weitgehendst vermieden wird.

Diese Aufgabe wird dadurch gelöst, daß die Reaktionsgase stromab des Katalysatornetzes vor der Kühlung über einen temperaturstabilen Katalysator für die Umwandlung des in den Reaktionsgasen enthaltenen N_2O geführt werden.

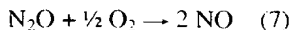Die Umwandlung kann je nach gewähltem Katalysator durch Zersetzung in die Elemente Stickstoff und Sauerstoff:

$$2\,N_2O \rightarrow 2\,N_2 + O_2 \quad (5)$$

oder durch Oxidation:

$$2\,N_2O + 3\,O_2 \rightarrow 4\,NO_2 \quad (6)$$

oder

$$N_2O + \tfrac{1}{2}\,O_2 \rightarrow 2\,NO \quad (7)$$

erfolgen.

Die Umwandlung durch Oxidation des N_2O zu NO oder NO_2 führt zu einer Umsatzsteigerung der Salpetersäureproduktion und wird daher bevorzugt.

Lachgas gehört zwar zu den sogenannten endothermen Verbindungen und sollte daher schon bei Raumtemperatur in die Elemente zerfallen, jedoch erfolgt die Zersetzung aber aus kinetischen Gründen erst bei Erwärmung. Die erfindungsgemäße Verfahrensführung nutzt in vorteilhafter Weise die Wärme der Reaktionsgase unmittelbar nach der NH_3-Verbrennung. Eine separate Erwärmung der Reaktionsgase für die N_2O-Umwandlung ist nicht erforderlich. Es wird vorzugsweise ein hochaktiver Katalysator eingesetzt, da die Verweilzeit der Reaktionsgase nach Austritt aus dem Katalysatornetz bis Eintritt in die Wärmetauscher kurz ist,

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damit eine thermische Zersetzung des sich gemäß Gleichung (1) bildenden NO in seine Elemente nicht begünstigt wird.

Weiterhin ist dafür Sorge zu tragen, daß der Katalysator zur N_2O-Umwandlung die gleichzeitig mögliche Reaktion einer NO-Zersetzung nicht bzw. nicht nennenswert beschleunigt.

Es ist bekannt, zur gleichmäßigen Beaufschlagung des der Abkühlung der Reaktionsgase dienenden Wärmetauschers bzw. Heizflächen die Reaktionsgase dem Katalysatornetz über eine Einrichtung zur Strömungsgleichverteilung zu führen, z. B. über eine Schüttung von Raschig-Ringen. Bei der erfindungsgemäßen Verfahrensführung kann der N_2O-Umwandlungskatalysator auch in Form von Raschig-Ringen oder dergleichen ausgebildet werden, um neben der N_2O-Umwandlung zugleich eine Strömungsvergleichmäßigung zu gewährleisten.

Auch ist es bekannt, das Platinnetz zu seiner Abstützung auf keramischen Elementen aufliegen zu lassen. Es liegt im Rahmen der bevorzugten Erfindungsführung auch solche Abstützelemente aus einem katalytisch aktiven Material für die N_2O-Umwandlung aufzubauen.

Es ist also zweckmäßig, daß die Reaktionsgase durch eine Schüttung von Katalysatorelementen oder über einen gasdurchlässigen Formkatalysator, wie z. B. Wabenkatalysator, geführt werden.

Vorzugsweise wird ein Katalysator ausgewählt aus der Gruppe: Edelmetall oder Keramik.

Wiederum bevorzugt wird der Einsatz einer Keramik, die mit Metallen, wie z. B. V, Cr, Fe, Ni, Co, Cu, Bi, Ca, Zn, Al, Mg, und/oder deren Oxiden und/oder Edelmetallen dotiert ist. In besonders bevorzugter Weise werden Tonkeramiken, d. h. Keramiken auf Aluminiumsilikat-Basis eingesetzt, weiter bevorzugt Cordierite.

Weiterhin ist es denkbar, als Katalysator Spinelle und/oder Perowskite einzusetzen.

Bei allen eingesetzten Katalysatoren muß dafür Sorge getragen werden, daß sie der Wärmebelastung im Bereich von 800 bis 1000°C unmittelbar nach Austritt der Reaktionsgase aus dem Katalysatornetz standhalten können.

Es kann entweder das reine Katalysatormaterial eingesetzt werden oder Katalysatormaterial wird auf einen ebenfalls temperaturstabilen Träger aufgebracht.

Die Erfindung richtet sich auch auf eine Vorrichtung zur Herstellung von Salpetersäure mit einem Reaktor, mindestens einem sich quer zum Reaktorinneren erstreckenden Katalysatornetz und mindestens einer dem Katalysatornetz nachgeschalteten Heizfläche.

Erfindungsgemäß ist dabei vorgesehen, daß zwischen dem Katalysatornetz und der Heizfläche ein gasdurchlässiger temperaturstabiler Katalysator für die Umwandlung von in den Reaktionsgasen enthaltenem N_2O angeordnet ist.

Dabei ist es zweckmäßig, wenn der Katalysator gleichzeitig der Strömungsgleichverteilung dient bzw. das Katalysatornetz für die NH_3-Verbrennung abstützt.

Eine erfindungsgemäße Vorrichtung soll nun anhand der beigefügten Figuren näher erläutert werden.

In den Reaktor 1 wird über eine Zuleitung 2 eine Mischung aus NH_3 und sauerstoffhaltiger Luft O_2 eingeleitet. Die Zuleitung 2 mit relativ geringem Querschnitt geht in eine Haube 3 größeren Querschnittes über, an die sich ein zylindrischer Behältergrundkörper 4 anschließt. Quer über die Eintrittsöffnung des Grundkörpers 4 erstrecken sich Platinnetze 5, die gegebenenfalls noch abgestützt sind. Unmittelbar nach den Platinnetzen ist ein Katalysatoreinbau 6 für die N_2O-Umwandlung angeordnet, der aus einer Schüttung von katalytisch aktiven Raschig-Ringen 6a und einem die Schüttung tragenden Lochblech 6b besteht. Die aus dem Ka-

talysatoreinbau 6 austretenden Reaktionsgase R treten in einen nur schematisch dargestellten Kühlflächeneinbau 7 ein, der von einem Kühlmittel K durchströmt wird. Die Reaktionsgase werden über einen Auslaß 8 abgezogen.

Patentansprüche

1. Verfahren zur Herstellung von Salpetersäure, bei dem Ammoniak an mindestens einem Katalysatornetz, insbesondere Platinnetz, unter Zufuhr Sauerstoff verbrannt wird und die Reaktionsgase gekühlt werden, **dadurch gekennzeichnet**, daß die Reaktionsgase stromab des Katalysatornetzes vor der Kühlung über einen temperaturstabilen Katalysator für die Umwandlung des in den Reaktionsgasen enthaltenen N_2O geführt werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß ein Katalysator für die Oxidation des N_2O eingesetzt wird.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet daß ein Katalysator für die Zersetzung des N_2O eingesetzt wird.

4. Verfahren nach mindestens einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Reaktionsgase über eine Schüttung von Katalysatorelementen geführt werden.

5. Verfahren nach mindestens einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Reaktionsgase über einen gasdurchlässigen Formkatalysator, wie z. B. Wabenkatalysator geführt werden.

6. Verfahren nach mindestens einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Reaktionsgase über einen Katalysator ausgewählt aus der Gruppe: Edelmetall oder Keramik geführt werden.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß eine Keramik eingesetzt wird, die mit Metalloxiden und/oder mit Metallen dotiert ist.

8. Verfahren nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß als Katalysator Tonkeramiken eingesetzt werden.

9. Verfahren nach mindestens einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß als Katalysator Spinelle und/oder Perowskite eingesetzt werden.

10. Verfahren nach mindestens einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß bei Temperaturen von 800 bis 1000°C temperaturstabile Katalysatoren eingesetzt werden.

11. Vorrichtung zur Herstellung von Salpetersäure mit einem Reaktor mindestens einem sich quer zum Reaktorinneren erstreckenden Katalysatornetz und mindestens einer dem Katalysatornetz nachgeschalteten Heizfläche, dadurch gekennzeichnet daß zwischen dem Katalysatornetz (5) und der Heizfläche ein gasdurchlässiger temperaturstabiler Katalysator (6; 6a, 6b) für die Umwandlung von in den Reaktionsgasen enthaltenem N_2O durch Zersetzung oder Oxidation angeordnet ist.

12. Vorrichtung nach Anspruch 11, dadurch gekennzeichnet, daß der Katalysator gleichzeitig der Strömungsgleichverteilung dient.

13. Vorrichtung nach Anspruch 11 oder 12 dadurch gekennzeichnet, daß der Katalysator gleichzeitig das Katalysatornetz für die NH_3-Verbrennung abstützt.

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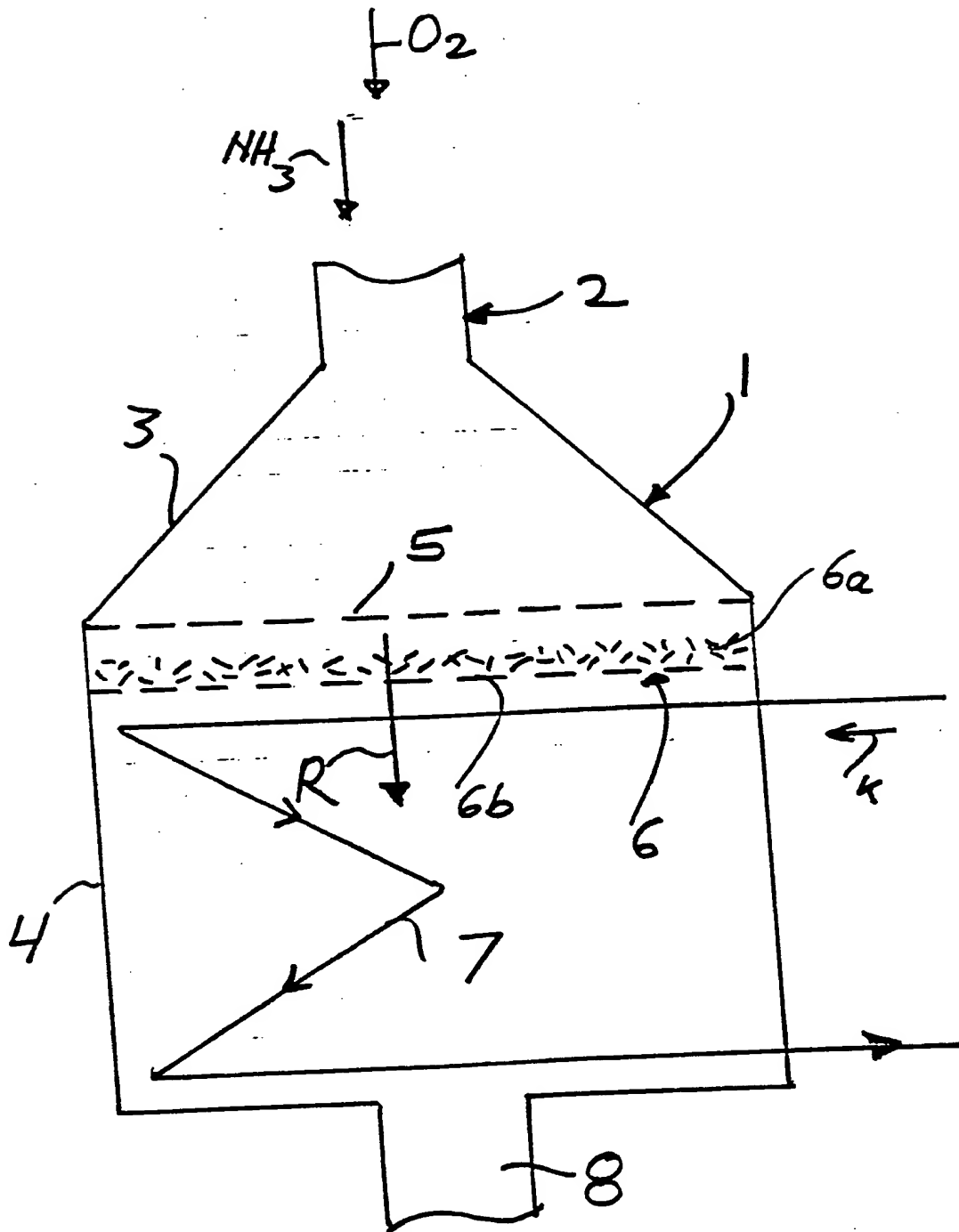
O_2

NH_3

2

1

3

5

6a

R

6b

6

K

4

7

8

(12)
EUROPEAN PATENT APPLICATION

(72) Inventor : Riley, Brian W., UOP Limited
Jeffrey's Road
Brimsdown, Middlesex EN3 7PN (GB)
Inventor : Richmond, John
High Beach
Essex 1G10 4AP (GB)

(74) Representative : Brock, Peter William et al
URQUHART-DYKES & LORD 91 Wimpole
Street
London W1M 8AH (GB)

(54) Process for controlled N2O decomposition in an N2O-containing gas stream.

(57) The exothermicity attending decomposition of N_2O to nitrogen and oxygen can lead to a multiplicity of process difficulties associated with high process temperatures. The process of the invention solves three difficulties by cooling a portion of the exit gases depleted in N_2O from the decomposition zone and then recycling at least a portion of the resulting cooled gas stream to the N_2O-decomposition zone. The process is amenable to process control to afford a very stable process largely independent on the particular catalyst used for N_2O decomposition. Where the N_2O-containing waste gas stream also contains NO_x, it is often highly desirable to pretreat the stream to remove NO_x prior to the N_2O-decomposition zone.

EP 0 564 144 A1

BACKGROUND OF THE INVENTION

Nitrous oxide, N_2O, frequently referred to as laughing gas, recently has been increasingly investigated as an undesirable component of gaseous emissions. Although formed in nature from bacterial action in soils and oceans, the levels associated with such "natural" emissions are not an environmental concern, a concern which arises in part from its relative unreactivity contributing to ozone layer depletion, and in part from its acting as a greenhouse gas, analogous in effect to carbon dioxide but far more potent. However, atmospheric levels of N_2O are found to be increasing bringing with it increased concern for its accumulation. One small but significant source of N_2O is that of adipic acid manufacture, where N_2O formation accompanies the nitric acid oxidation of cyclohexanone. Exit gases from the aforementioned reaction may contain quite high concentrations (about 30 volume percent) of N_2O and are discharged directly into the atmosphere. Off gases from nitric acid plants also are being recognized as a source of N_2O, although perhaps in significantly lower exit gas concentration, but nonetheless in substantial total amounts. Other N_2O-emission sources are the manufacture of hydroxylamine derivatives, caprolactam production, and the low temperature combustion of nitrogen-containing materials, as in fluid bed incinerators. With increasing global environmental sensitivity generally, and with more stringent local requirements particularly, there has arisen a need for implementing a process for N_2O destruction which addresses the concerns attached to emissions containing substantial amounts and/or concentrations of N_2O.

Several catalyst systems are known to effect the decomposition of nitrous oxide to nitrogen and oxygen. However effective these may be, some inherent characteristics of nitrous oxide decomposition largely independent of the particular catalyst system used introduce complexities which the process of this invention addresses. In particular, even though N_2O decomposition is a highly exothermic reaction, whose heat of reaction is approximately 19.5 kcal mole^{-1}, its decomposition is initiated by most catalytic systems at a temperature of several hundred degrees centigrade. Where the catalyst is used as a solid bed, the large reaction exotherm coupled with a high space velocity of the N_2O-containing gas stream through the reactor means that there is a considerable temperature increase within and along the catalyst bed, an increase which easily can reach several hundred degrees centigrade. But such a large temperature increase across the catalyst bed cain have several adverse consequences. One potential detriment is sintering of the catalyst and/or catalyst support leading to a reduction of catalyst activity and a reduction in catalyst life. Another detriment is that many catalysts used for the decomposition of N_2O also can effect the reaction of nitrogen and oxygen to form NO_x. Thus, it is often desirable to have some maximum temperature, T_{max}, in the catalyst bed to avoid the foregoing detriments. This maximum temperature will depend primarily on the catalyst and should not be exceeded despite changes in the N_2O-containing feed, feed rate, the temperature necessary to initiate N_2O decomposition, and other reaction variables.

Although many ways are possible to ensure this outcome, it has now been found that a particularly effective means is to cool some portion of the effluent gas and to recycle the cooled effluent gas to one or more points along the path of the gas stream through the decomposition zone. By varying the amount of effluent gas recycled, the degree to which it is cooled, the points at which it is recycled to the decomposition zone, and/or feed flow rate, it is possible to maintain the temperature everywhere in the decomposition zone less than T_{max} while maintaining a high throughput of the N_2O-containing waste gases in the decomposition zone.

SUMMARY OF THE INVENTION

The purpose of this invention is to provide a process for controlled catalytic decomposition of N_2O where the exothermicity of the reaction is controlled so as to maintain temperatures within the decomposition zone under some predetermined maximum, T_{max}. In one embodiment a N_2O-containing gas stream is passed over a N_2O-decomposition catalyst in a N_2O-decomposition zone, and all or some part of the effluent gas from the decomposition zone is cooled and recycled to the decomposition zone in order to maintain all temperatures therein under T_{max}. In another embodiment signals representative of the flow rate of the gas stream entering the decomposition zone and of the temperature at at least one point within the decomposition zone, are used to control the amount of cooled effluent gas recycled to the decomposition zone, the degree of cooling effected, and the points within the decomposition zone to which the cooled effluent gas is recycled. Yet another embodiment incorporates a NO_x removal zone prior to the N_2O decomposition zone, especially where there is greater than 100 ppm NO_x in the N_2O-containing gas stream. Other embodiments will be apparent from the ensuing description.

DESCRIPTION OF THE FIGURES

Figure 1 is a process flow diagram for the invention.

Figure 2 shows a similar process flow diagram with associated process controls.

DESCRIPTION OF THE INVENTION

The process of the invention is depicted in Figure 1. In one aspect the process is one where a N_2O-containing gas, generally a waste gas stream, is passed into a catalytic decomposition zone which effects cleavage of N_2O into oxygen and nitrogen. At least a part of the effluent from the decomposition zone is then cooled, and some or all of the cooled effluent is recycled to the decomposition zone, acting as a diluent and/or as a coolant, but in any event causing a reduction in the temperature of the decomposition zone and maintaining it within the predetermined limits.

In another aspect the process is a controlled one for decomposing N_2O in a waste gas stream into nitrogen and oxygen using a solid catalyst in a decomposition zone, cooling at least a portion of the effluent gas from the decomposition zone, and recycling at least some of the cooled effluent gas to the decomposition zone. The temperature within the decomposition zone is measured at one or more locations, and the signal(s) provided by the temperature measuring means is then used, directly or otherwise, as input to a processor or computer operating according to a predetermined algorithm to control some combination of the waste gas feed rate, the amount of effluent gas cooled, the degree to which the effluent gas is cooled, the amount of cooled effluent gas recycled to the decomposition zone, and the location(s) within the decomposition zone to which it is recycled. The purpose of such control is to ensure that the temperatures within the decomposition zone are at all times and places below some predetermined maximum temperature T_{max} in order to maximize catalyst life, catalyst activity, and to minimize subsequent formation of NO_x within the decomposition zone where this is important.

The feedstocks which are used in the practice of the invention are generally N_2O-containing waste gases produced by one or more industrial processes and are susceptible to a very great diversity of composition. At one extreme the gas stream to be treated by the catalyst may be essentially pure N_2O. Such a case will be infrequent; more usually the gas stream contains up to 65 volume percent of N_2O, and even more typically does not contain more than 35 volume percent N_2O. In the most prevalent case the N_2O-containing gas stream also contains water, and in fact may be saturated with water vapor at the gas stream temperature. The amount of water present in the gas stream, even if at saturation, will depend on such factors as gas stream temperature, pressure, and pretreatment, if any. However, the water content is most likely to be in the range of 1-2 volume percent as a typical N_2O-containing waste gas stream contains water vapor in this amount.

The N_2O-containing gas stream generally, but not necessarily, also contains oxygen to the extent of at least 0.5 volume percent, more often in the range of 3-15 volume percent, and in extreme cases where the gas stream is at, e.g., 15 atmospheres (1621 kPa) pressure, may contain oxygen at a partial pressure up to about 3 atmospheres (304 kPa). The waste gas stream to be treated may also contain variable amounts of volatile organic compounds as well as other nitrogen oxides. The nature of the components in the gas stream other than N_2O is not of particular relevance so long as these components do not interfere with N_2O decomposition and do not adversely affect the catalyst used in the decomposition zone. Where the gas stream contains other oxides of nitrogen, the so-called NO_x, especially at concentrations above about 100 ppm, the process as described below may need to be modified as discussed hereinafter to remove NO_x prior to the N_2O-decomposition zone.

The feedstock is then passed into a decomposition zone containing a solid catalyst which effects the decomposition of N_2O into nitrogen and oxygen. Most such catalysts require a minimum temperature, T_{min}, below which N_2O decomposition is not effected. In one variant the feedstock is heated to a temperature of at least T_{min} to ensure reaction occurring even at the inlet of the decomposition zone, i.e., reaction occurs from the very start of the catalyst bed present in the decomposition zone. In another variant at least some part of the decomposition zone may be heated to at least T_{min} to initiate decomposition. Because of the high exothermicity of the reaction, once decomposition of N_2O has begun it generally generates sufficient heat to be self-sustaining, and not only is no further heating required but in fact cooling is needed to maintain all points within the decomposition zone at a temperature less than some predetermined maximum, T_{max}, which corresponds to the onset of catalyst sintering, NO_x formation, or some other deleterious and undesirable process.

It also needs to be mentioned that the minimum temperature initially needed to sustain the reaction along the catalyst bed may not be the same as that established at steady state conditions. Thus, it is observed with some regularity that a higher temperature, T_a, is required to initiate the decomposition of N_2O at start-up than the temperature, T_b, required to maintain the decomposition across the catalyst bed after the system is operating at a steady state, i.e., $T_a > T_b$, and sometimes $T_a >> T_b$.

The catalyst in the decomposition zone is a solid catalyst, and the decomposition zone itself is generally a reactor containing the catalyst as a bed or as a monolith. Although the most usual bed configuration is one where the catalyst is present as a fixed bed, configurations where the catalyst is present as a fluidized bed, an ebullating bed, a radial bed, and so on are within the scope of this invention. Except for operating details, it must be stressed that the practice and success of the process which is the invention is

independent of catalyst type and catalyst configuration.

Various kinds of materials have been utilized as solid catalysts for the decomposition of N_2O, but it appears possible to classify them into four categories; metal oxides, metals, zeolites, and a nondescript group encompassing a diversity of otherwise unrelated materials. For example, removal of nitrous oxide from gas using catalysts from group Ib or group VIII as their oxides is the subject of JP-A-63007862. In US-A-4,259,303, the catalyst comprised at least 1 metal oxide selected from the group consisting of ferric oxide, cobalt oxide, cupric oxide, chromium oxide, manganese dioxide and nickel oxide operated at a temperature of 250-650°C. US-A-3,459,494, the catalyst was an alkali metal oxide, an alkali metal silicate, ain alkaline earth metal oxide, an alkaline earth metal silicate, or mixtures thereof operated at a temperature above 700°C. JP-A-61153142 teaches that a catalyst of 75 weight percent Co_xO_y(y/x up to 1.5) with the remainder as copper and manganese oxides can be used as catalyst for decomposition of nitrogen oxides, including N_2O. GB-A-2059934 claims that N_2O is removed from waste anesthetic gas using a catalyst comprising at least one of ferric, cobalt, cupric, nickel and chromium oxides and manganese dioxide at 250-650°C.

Illustrative of the use of metals as N_2O catalysts is JP-B-86045487 which reports that N_2O in anesthetic gas is removed by passage through a catalyst composed of an iron family metal (iron, nickel, cobalt, etc.), a rare earth metal oxide, and a platinum family metal at 150-550°C. JP-B-86045486 teaches that a catalyst comprising at least one of platinum, palladium, rhodium, and iridium, and ruthenium effects decomposition at temperatures 150-550°C. Palladium on alumina has been used to effect >99% decomposition at 300-400°C and 5000 hr.$^{-1}$ gas hourly space velocity (GHSV) [Chem. Abst., 109(2): 11062s].

As an example of the use of zeolitic materials one can mention U.S. 4,507,271, which describes the removal of N_2O from gases containing hydrogen, NO, and N_2O by treatment with molecular sieves, preferably A-, X-, or Y-zeolites. L. M. Aparicio, J. Catal., 104, 381 (1987) studied the decomposition of N_2O in flowing helium at 800°K (527°C) and 1 atmosphere (101.3 kPa) using iron-exchanged, silicon-substituted Y zeolites as a catalyst. The decomposition of N_2O at 600-750°K and at initial nitrous oxide pressure of 60 mm Hg (8 kPa) was studied using certain cobalt/magnesium/alumina spinel solid solutions by C. Angeletti, J. Chem. Soc., Faraday Trans., 74, 1595 (1978). J. Leglise used iron-exchanged mordenite and compared his results with that obtained using iron Y-zeolites at temperatures apparently above about 250°C [Chem. Abst., 100(18): 145662k]. Mordenite-type zeolites exchanged by alkali and rare earth metals were studied

in the thermal decomposition of N_2O at 250-600°C by A. A. Slinkin [Chem. Abst., 97(20): 169727f].

SU-A-1011238 reports a catalyst for N_2O decomposition at 170°C with 99% efficiency contains calcium carbide, calcium oxide, sodium chloride, activated carbon, iron-silicon, aluminum chloride, magnesium chloride, manganese chloride, silicon carbide and calcium chloride. Copper (II) complexes of dibenzothiophenes and carbazoles have been used for thermal decomposition of N_2O at 483-533K; SU-A-1237248-A.

Another catalyst which may be used in the invention is one composed of a first metal oxide as a support on which is dispersed a second metal oxide. The first metal oxide used as a support is a refractory inorganic oxide which is either tin((IV) or a rare earth metal oxide, where the rare earth is that of atomic number 57-71, or any combination thereof. The rare earth metals are preferred as the metal(III) oxides except for cerium(IV) oxide. Favored among the rare earth metal oxides are those of cerium(IV), lanthanum(III), praesodymium(III), erbium(III), thulium(III), yterbium(III), and lutetium(III), with cerium(IV) and lanthanum(III) oxides particularly recommended. The oxides used were rather low surface area materials, and it was quite unexpected that they showed unique qualities as a support in this invention. Although other oxides were extensively examined as a support, catalysts using them showed hysteresis and/or were deactivated in the presence of water and/or oxygen. Although it is uncertain why tin and the rare earth metal oxides are so unique, it appears that they exhibit strong metal-support interactions with the second metal oxides dispersed on them. S. J. Tauster et al., Science, 211, 1121 (1981); US-A-4,149,998. Among the foregoing tin(IV) oxide is particularly desirable as a support, especially from a cost and availability standpoint.

The tin or rare earth metal oxide of the preferred catalyst used in the instant invention may be used in any configuration, shape or size which exposes the tin or rare earth metal oxide and any other catalytic components dispersed thereon to the gas to be treated. For example, the tin or rare earth metal oxide can be conveniently employed in particulate form, the tin or rare earth metal oxide can be deposited onto a solid monolithic carrier, or the monolith may be extruded or formed as the tin or rare earth oxide. When a particulate form is desired, the tin or rare earth metal oxide can be formed into shapes such as pills, pellets, granules, rings, spheres, etc. The particulate form is especially desirable where large volumes of catalysts are needed, and for use in circumstances in which periodic replacement of the catalyst may be desired. In circumstances in which less mass is desirable or in which movement or agitation of particles of tin or rare earth metal oxide may result in attrition, dusting and resulting loss of dispersed metals or undue increase

in pressure drop across the particles, a monolithic form is preferred.

In the employment of a monolithic form, it is usually most convenient to employ the tin or rare earth metal oxide as a thin film or coating deposited on an inert carrier material which provid s the structural support for said tin or rare earth metal oxide. The inert carrier material can be any refractory material such as ceramic or metallic materials. It is desirable that the carrier material be unreactive with the catalytic components and not be degraded by the gas to which it is exposed. Examples of suitable ceramic materials include silica, sillimanite, petalite, cordierite, mullite, zircon, zircon mullite, spodumene, alumina-titanate, etc. Additionally, metallic materials which are within the scope of this invention include metals and alloys as disclosed in US-A-3,920,583.

The monolithic carrier material can best be utilized in any rigid unitary configuration which provides a plurality of pores or channels extending in the direction of gas flow. The configuration may be a honeycomb, foam, or planar catalyst configuration or in any other form which affords a high surface area. The structures can be used advantageously in either unitary form, or as an arrangement of multiple modules. The honeycomb structure, for example, is usually oriented such that gas flow is generally in the same direction as the cells or channels of the honeycomb structure.

If a particulate form is desired, the tin or rare earth metal oxide can be formed into granules, spheres or extrudates by means well known in the industry. For example, a tin or rare earth metal oxide powder can be combined with a binder such as a clay and rolled in a disk pelletizing apparatus to give tin or rare earth metal oxide spheres. The amount of binder can vary considerably but for convenience is present in an amount generally from 10 to 30 weight percent.

A second metal oxide is dispersed on the support, where the second metal oxide is palladium oxide, platinum oxide, iridium oxide, ruthenium oxide, osmium oxide, gold oxide, indium(III) oxide, rhodium oxide, or any combination of them, at atypically high concentrations affording from 0.05 up to 25 weight percent of the finished catalyst expressed as the metal, exclusive of monolith, if any. However, concentrations in the range of 1-18 weight percent are preferred, with those in the range of 3-15 weight percent even more highly preferred, especially where NO_x formation is to be avoided. Palladium and, to some extent, rhodium are somewhat preferred over platinum, and a particularly desirable catalyst is one where the support is tin(IV) oxide bearing palladium oxide, especially where the latter is at a concentration to give 1-18 weight percent palladium.

The aforedescribed catalysts also may be promoted by various cations, especially those of the alkali and alkaline earth metals. Thus, increased cata-

lyst activity often results from the presence of one or more of sodium, lithium, potassium, magnesium, calcium, barium, and strontium cations, in any combination, typically present in a total amount from about 0.1 to about 10 weight percent based on the finished catalyst (exclusive of monolith). Preference among the foregoing cations is given to lithium, magnesium and calcium. Tungsten(IV) oxide, lead oxide, bismuth oxide, and tin(II) oxide also may be useful as a promoter.

The preparation of these catalysts can be by any of the methods known to the skilled worker. For example, tin oxide may be impregnated with the requisite amount of a second metal salt, as by contacting the support with an aqueous solution containing the desired amount of the metal salt, rolling the mixture while evaporating the water, and finally drying the impregnated support at a temperature in the range of, e.g., 110-150°C. The dried impregnated support then may be calcined in air, often at a temperature in the range of 300-400°C, to convert the second metal to its oxide and provide the finished catalyst which may be reduced or used directly without any further treatment.

In a preferred embodiment the second metal oxides are present largely at or near the surface of the first metal oxide support. That is, the first metal oxides are not uniformly dispersed throughout the bulk of the support but instead are preferentially concentrated in a shallow layer at and near the support surface. Such selective surface impregnation or concentration may be achieved by any means generally available and include using co-additives such as thioacetic acid, spray coating with restricted volumes of metal-containing solution, impregnation of pore-filled support (obtained by presoaking in a suitable liquid) with a metal-containing solution, and selective metal precipitation, to name but a few. See US-A-4,519,951.

Especially where the feedstock contains high concentrations of N_2O the exothermicity of the latter's decomposition results in a temperature within at least one portion of the decomposition zone sufficiently high to effect catalyst sintering or to bring about oxidation of nitrogen to higher nitrogen oxides, NO_x, which may be undesirable. It is for these reasons that at least a portion of the effluent gases depleted in N_2O and enriched in nitrogen and oxygen are directed to a cooling zone. It is important to understand that the process does not need to be carried out so that all of the N_2O is decomposed in the decomposition zone, or that the effluent gases from the decomposition zone be essentially devoid of N_2O.

At least a portion of the effluent from the decomposition zone is cooled in a cooling zone. The amount of effluent gas which is cooled and the degree of cooling is a function of feedstock, catalyst, feed rate, operating conditions generally, and reactor design. What is needed is to cool some portion of effluent suf-

ficiently so that upon its recycle to the decomposition zone it will ensure that at all points within the decomposition zone the temperature does not exceed T_{max}. Even though it is not feasible to give the amount of effluent cooled and its degree of cooling in closed form as a function of the requisite independent variables, it is well within the purview of one skilled in the art of process control to determine these factors for any particular situation.

The cooled effluent gases, in whole or in part, are then recycled to at least one point within the decomposition zone. For example, one might recycle only a portion of the cooled effluent gases and use the remaining portion to mix with uncooled effluent gas before its discharge into the atmosphere. On the other hand all of the cooled effluent gas may be recycled and the uncooled effluent gas may be separately cooled in a second cooling zone prior to discharge. The variants are largely a matter of choice, or they may be dictated by other constraints placed on the process, but in all events they are well within the skill of the ordinary person in the art.

Where the N_2O-containing feed gas stream also contained NO_x, particularly at concentrations above about 50 ppm, and especially above about 100 ppm, the effectiveness of many catalysts for N_2O decomposition is significantly impaired. Thus, when the gas stream to be treated also contains NO_x one frequently observes a substantial decrease in catalyst activity, which necessitates an analogous decrease in gas hourly space velocity or an increase in operating temperature where possible, in order that the desired degree of N_2O decomposition be maintained. Alternatively, one might experience a substantial decrease in catalyst lifetime, necessitating more frequent catalyst regeneration and/or replacement. In these cases it is highly desirable to remove NO_x in a zone prior to the N_2O-decomposition zone. The removal of NO_x from various kinds of waste gases is a well known process practiced in many variants and needs no extensive discussion. See, e.g., Kirk-Othmer, "Encyclopedia of Chemical Technology," 3rd Edition, Vol. 9, pp. 527-30. One quite highly preferred variant is the selective reduction of NO_x with ammonia in the presence of oxygen, often catalyzed by precious metals. In this variant, which is particularly suitable in the practice of the invention, any excess ammonia exiting the NO_x-decomposition zone and entering the N_2O-decomposition zone will not be harmful to most of the N_2O-decomposition catalysts and in fact will itself be decomposed in the N_2O-decomposition zone, with the quite desirable consequence that the gaseous effluent discharged into the atmosphere does not have to be separately treated to remove ammonia.

The invention may perhaps be better understood with reference to Figure 1, which represents the process flow and illustrates how the invention may be better practiced. Feedstock 1 is the N_2O-containing

waste gas stream. Where it also contains NO_x, particularly at concentrations above about 50 ppm and especially above 100 ppm, it is first directed to a NO_x-removal zone 2, where the dotted lines indicate this is an optional zone whose presence or use will be dictated by the amount of NO_x in 1 as well as the particular catalyst used for N_2O decomposition. Stream 7 is then the effluent from the NO_x-removal zone or, where such zone is absent, feedstock 1. Stream 7 enters the N_2O-decomposition zone 14 containing a suitable N_2O-decomposition catalyst and where N_2O is catalytically decomposed into N_2 and O_2 and whose effluent gases, depleted in N_2O, exit at 20. The gas stream is then split into the discharge stream 25 and a stream 28 which is passed into cooling zone 30. The stream 28 is cooled within zone 30 to a temperature or by an amount suitable to moderate the exothermic N_2O decomposition as determined by the process design variables. The cooled exit gases from 30 are then recycled, in whole or in part, as indicated by stream 55, with the remainder if any discharged in stream 50. The cooled gas stream 55 is recycled to the decomposition zone 14 either by combination with stream 7, by entering the decomposition zone at a point different from the entry point for stream 7, or any combination of these.

Figure 2 illustrates one particular type of control system configuration which may be used in the invention, but it will be recognized that the invention extends to different types of control system configurations which accomplish the same purpose in essentially the same way and with essentially the same results. Process flow is given by heavy lines and flow direction is indicated by the bolded arrows. Signals are indicated by normal lines, with normal arrows indicating the direction of signal transmission. Transducers are given as circles having two-letter designations ending in X, and controllers are circles having two-letter designations ending in C. Generally the signals provided by any transducer will be electrical in form and may be either analog or digital. For simplicity any transducer for analog-digital conversion is omitted, as is any transducer for conversion of pneumatic, mechanical, or hydraulic signals to electrical signals. For generality the figure is drawn so that each sensing means or sensor, uniformly designated by the symbol "||", is separate from its transducing means or transducer, but it needs to be recognized that in many cases the sensing means and transducing means are congruent, i.e., one device performs both functions, as is the case for example with a thermocouple or thermistor.

Referring to Figure 2, the feedstock designated as 1 is either the waste gas stream or the effluent from the NO_x-removal zone if one is present. Flow sensor 3 in combination with transducer 5 provides a signal representative of the feedstock flow rate as input to computer or processor 40. Conditions within

the decomposition zone **14** are such as to decompose N_2O into nitrogen and oxygen, which means that at some point within the decomposition zone the temperature must be sufficient to ensure and sustain N_2O decomposition. At least one, and usually a multiplicity, of temperature sensing means is placed within the decomposition zone and each in conjunction with its transducer provides a signal representative of the local temperature in the environs of the temperature sensing means. The figure shows four sensors and four transducers TX - **10, 11, 12,** and **13** - but it needs to be understood that this number is arbitrary. The sole constraint is that at least one temperature sensing means-transducing means combination is necessary. Each temperature sensor-transducer signal is used as a separate input to the computer or processor.

Hot effluent gases exit the decomposition zone at **20** and the effluent gas stream is split by flow controlling means (flow controller) **23** into a discharge stream **25** and a stream **28** flowing into the cooling zone **30**. The amount of heat removed from stream **28**, i.e., the degree of cooling effected in cooling zone **30**, is controlled by the temperature controlling means (temperature controller) **35**. Another temperature sensing means-transducing means combination **45** provides a signal representative of the temperature of the cooled effluent gas stream **47**, and this signal is also used as input to **40**. The effluent gas stream is then split into a discharge stream **50** and a recycle stream **55** by flow controller **60**.

The computer or processor **40** receives as input at least the signals provided by each sensor in conjunction with its transducer. These signals are representative, for example, of the feedstock flow rate, the temperature at various points along the decomposition zone, and the temperature of the cooled effluent gas stream. Using an algorithm based on such variables as the reactor design, the exotherm generated by the particular waste gas stream, the feed rate of the waste gas stream into the decomposition zone, the specific catalyst used, the heat loss from the decomposition zone, and so on, the computer or processor will generate output signals to various controllers whose net effect is to maintain the temperature at all points within the decomposition zone within predetermined limits.

For example, output signal **65** is provided to flow controller **23** and determines what fraction of the effluent gases exiting from the decomposition zone **14** is passed into the cooling zone **30**. Output signal **70** is provided to temperature controller **35**, which determines the amount of heat removed from the effluent gas stream **28** entering cooling zone **30**. A separate output signal **75** is sent to flow controller **60** which acts essentially as a stream splitter for the cooled effluent gases exiting cooling zone **30**. Flow controller **60** recycles all or part of the effluent gas stream as recycle

stream **55** with the remaining portion being discharged as stream **50**.

The cooled effluent gas stream **55** is recycled to the decomposition zone **14** and/or to the N_2O-containing waste gas stream **1** used as the feedstock for the process. Figure 1 has illustrated two recycle points within the decomposition zone but it will be recognized that the number is arbitrary. That is, it may be largely a matter of design choice whether the cooled effluent gas stream is recycled only to the incoming feed gas stream **1**, whether it is recycled only to the decomposition zone **14**, or whether it is recycled to both the feedstock and the decomposition zone. If the cooled effluent gas stream is recycled to decomposition zone **14**, it is largely a matter of design choice as to where within the decomposition zone the recycled gas enters and how many recycle entry ports are present. In any event, output signals **80, 85,** and **90**, which are provided to flow controllers **95, 100,** and **105**, resp., act in combination to direct the cooled effluent gas stream **55** to those points predetermined to be most effective for the particularities of the process at hand.

Claims

1. A process for the controlled decomposition of N_2O in a gas stream containing N_2O comprising:
    a) passing the N_2O-containing gas stream [7] into a catalytic N_2O-decomposition zone [14], having a permissible maximum temperature of T_{max}, where said N_2O-containing gas stream is brought into contact under N_2O-decomposition conditions with a catalyst effecting decomposition of N_2O into nitrogen and oxygen to afford an effluent gas stream [20] depleted in N_2O and enriched in nitrogen and oxygen;
    b) cooling at least a portion of the effluent gas stream [28] to afford a cooled effluent gas stream [50]; and
    c) recycling at least a portion of the cooled effluent gas stream [55] to the N_2O-decomposition zone [14] so as to maintain all temperatures in the N_2O-decomposition zone [14] below T_{max}.

2. The process of Claim 1 further characterized in that the temperature at at least one point within the N_2O-decomposition zone [14] is measured and the temperature of the zone controlled by means of a predetermined algorithm using the measured temperature, and
    (a) the rate of passing the N_2O-containing gas stream [7] into the N_2O-decomposition zone [14], or
    (b) the degree of cooling of the portion of the

effluent gas stream [28], or

(c) the amount of cooled effluent gas stream [55] recycled to the N_2O-decomposition zone [14], or

(d) any combination thereof, where said algorithm maintains all temperatures in the N_2O-decomposition zone [14] below T_{max}.

3. The process of Claim 1 or 2 where the N_2O-containing gas stream [7] has been subjected to an NO_x-removal step prior to passage into the N_2O-decomposition zone [14].

4. The process of Claim 1, 2 or 3 where the N_2O-containing gas stream contains N_2O at a concentration up to 65 volume percent.

5. The process of any one of Claims 1 to 4 where the N_2O-containing gas stream contains N_2O at a concentration up to 35 volume percent.

6. The process of any one of Claims 1 to 5 further characterized in that the gas stream also contains water.

7. The process of any one of Claims 1 to 6 further characterized in that the gas stream also contains oxygen at a concentration of at least 0.5 volume percent.
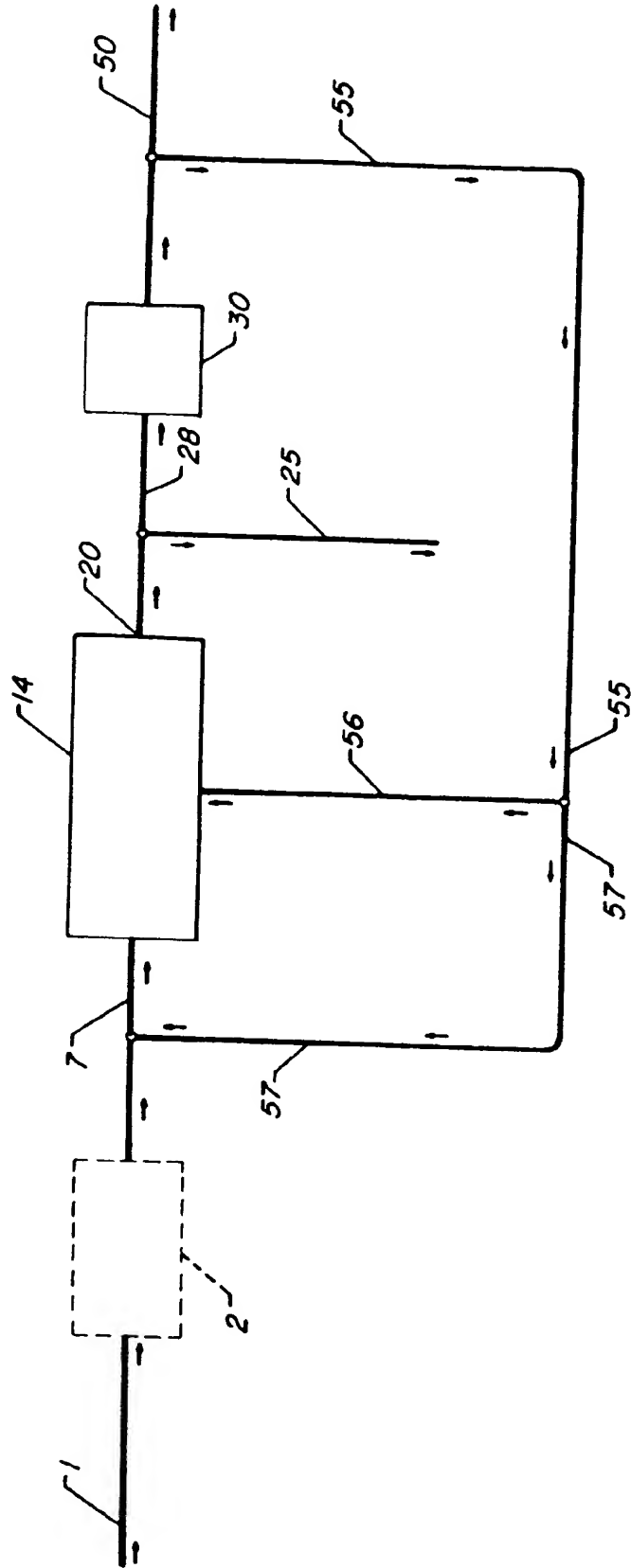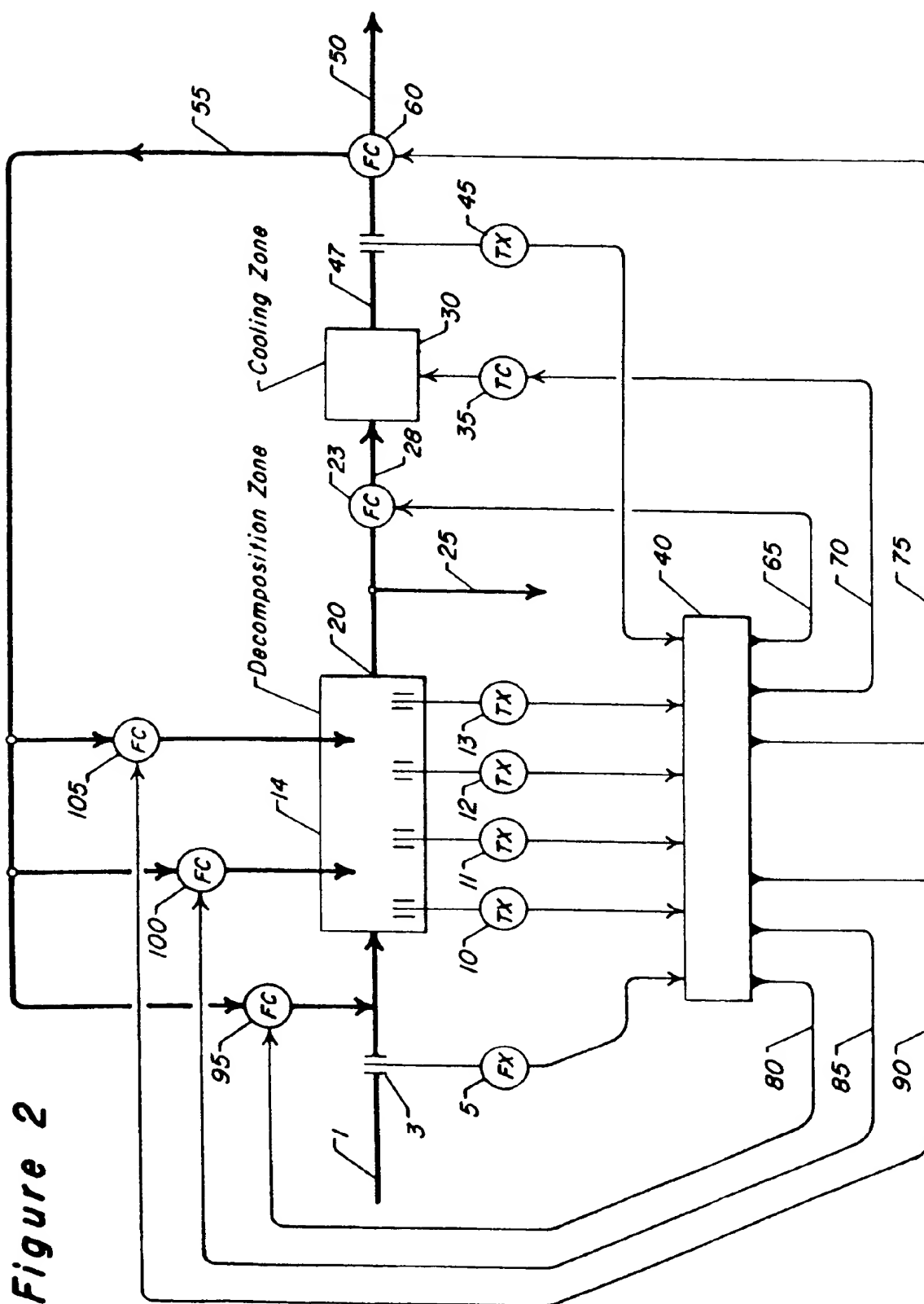
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Figure 1

Figure 2

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 2175

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 176 (E-749)25 April 1989 & JP-A-10 05 090 (MITSUBISHI HEAVY IND LTD) 10 January 1989 * abstract *	1	B01D53/36
Y	FR-A-2 160 427 (ENGELHARD MIN & CHEM CORP) * page 3, line 2 - line 24 * * page 4, line 29 - page 5, line 2; figure 1 *	1,2,6,7	
Y	PATENT ABSTRACTS OF JAPAN vol. 1, no. 166 (C-77)(3689) 27 December 1977 & JP-A-52 107 269 (MITSUBISHI KASEI KOGYO KK) 8 September 1977 * abstract *	1,2,6,7	
A	EP-A-0 199 186 (LINDE AG) * page 6, line 8 - line 12; claims 1-7; figure 1 *	1,6,7	
A	EP-A-0 415 306 (NONOX KAT AG) * column 4, line 38 - column 6, line 6; figure 1 *	1,6,7	TECHNICAL FIELDS SEARCHED (Int. Cl.5) B01D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 JULY 1993	EIJKENBOOM T.

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